

Link of the Light-induced Structural Changes and the Conductivity Changes in Hydrogenated Amorphous Silicon — a Two-domain Model

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ABSTRACT

A phenomenological model for the light-induced metastability of a-Si:H is proposed in which a two-domain amorphous network plays a central role. Boundaries between high- and low-density domains are associated with a significant fraction of the clustered Si-H. Weakly bonded hydrogen at these boundaries is mobilized by non-radiative carrier recombination and catalyzes metastable configuration changes in the Si network. This gives rise to the observed volume expansion and could play a role in electronic defect creation.

INTRODUCTION

The SWE [1] in a-Si:H describes the decrease of conductivity and photoconductivity due to the increase of silicon dangling bond (DB) concentration upon light soaking. After two decades, the light-induced structural changes were found. i.e. the volume expansion on the order of 10^{-5} of the initial values.[2] How are the different mechanisms linked? We present a phenomenological model.

MODEL

a-Si:H is known to be inhomogeneous on the nanometer scale.[2,3] ^1H NMR studies have concluded that there are 20-70% volume fractions in a-Si:H that contain little or no hydrogen.[3] If we assume that such H-free regions comprise high-order domains with density ρ_{high} , and the remainder is a low-order matrix with density ρ_{low} , then the 2% variation of measured mass densities yield the following estimates: $\rho_{\text{high}} \approx 2.31 \text{ g/cm}^3$, $\rho_{\text{low}} \approx 2.23 \text{ g/cm}^3$. Clearly an interface between such domains, on the scale of angstroms, will have a very large density gradient. Such abrupt changes in local order will also lead to large interfacial strain, characterized by weak Si-Si bonds, that is relieved somewhat by a high concentration of bonded hydrogen. Figure 1 shows a schematic 1-D model of a spatially modulated mass density profile that contains the three regions. The δ 's represent the spatial extents of the regions. The size of the high-density domain is estimated to be $\sim 20\text{--}30 \text{ \AA}$ from variable-coherence TEM [4], and thus the conventional film would have low-density domains of average size $80\text{--}120 \text{ \AA}$. The domain boundary is assumed to be $\sim 10 \text{ \AA}$ or less.

It is well known that the majority of the clustered H in a-Si:H evolves at lower temperature than the dilute H, and therefore we propose that such domain boundary regions contain a significant fraction of the weakly bound, clustered H. In the presence of non-radiative carrier recombination, a

multiphonon process, a subset of the weakly-bound H is expected to be locally mobile. This is suggested by a multiple-quantum NMR study that has revealed rearrangement of cluster configurations at temperatures below the hydrogen evolution temperature range (of energy $\sim 0.05 \text{ eV}$) [5], whereas the energy released by a recombination event is 1.1 eV . When weakly bound H is mobilized locally, it can sometimes catalyze or stabilize local configurational changes of neighboring Si atoms. This process can be considered thermodynamically as an entropic process, where the net effect is increased disorder. Increased disorder corresponds to a decrease in average density, i.e. increase in volume. Underlying the motion are metastable configurational changes at microscopic sites in the Si network that correspond to less ordered, higher energy states. Given that the overall change is sufficiently small, suitable annealing is expected to completely reverse the *average* motion, whereas the detailed local motions are probably seldom reversible.

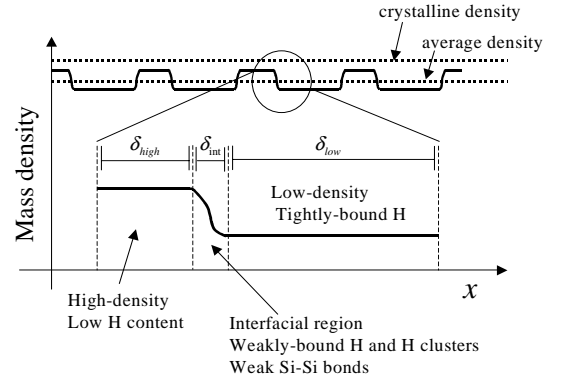


Fig. 1. Spatially modulated mass density profile in one dimension.

ANALYSIS

In the context of this picture, the order of magnitude of the changes required to account for the observed volume expansion can be estimated. The expression

$$\bar{\rho} = \rho_{\text{high}} v_{\text{high}} + \rho_{\text{low}} v_{\text{low}} + \bar{\rho}_{\text{int}} v_{\text{int}}, \quad (1)$$

is the measured mass density, with the average density at

the domain boundary $\bar{\rho}_{\text{int}} \approx \frac{\rho_{\text{high}} + \rho_{\text{low}}}{2}$ and $\sum v = 1$

(v 's are domain and boundary volume fractions and the bar denotes average density). Then, taking into account small boundary motions of the types shown schematically in figure 2, the fractional change in (one-dimensional) film density $\bar{\rho}$ is given approximately by

$$\frac{\Delta\bar{\rho}}{\bar{\rho}} \approx \frac{\rho_{high}-\rho_{low}}{\rho_{high}+\rho_{low}}(\Delta v_{high}-\Delta v_{low}) \approx \frac{\rho_{high}-\rho_{low}}{\rho_{high}+\rho_{low}}\left(\frac{2\gamma_1+\gamma_2}{\delta_{low}+\delta_{high}+\delta_{int}}\right), \quad (2)$$

where γ_1 is the distance of domain boundary propagation and γ_2 is the amount of its extension. Since $\frac{\Delta V}{V} = \frac{-\Delta\bar{\rho}}{\bar{\rho}} \sim 10^{-5}$ [6], the densities and sizes estimated above for the high- and low- order regions can be inserted into equation 2 to yield $2\gamma_1 + \gamma_2 \approx 0.07$ Å. Therefore, as an order of magnitude estimate, only a few percent of all domain boundaries need to move ~ 1 Å in order to produce the maximum volume expansion has been measured, a small change indeed. Furthermore, it is reasonable that $\sim 1\%$ of these metastable sites could produce DB's or other electronic defects, consistent with the magnitude of the defect density. Rather than proposing a specific microscopic mode of defect creation, this model only localizes the metastable changes in or near domain boundaries, and asserts that a small fraction of local structural changes associated with the volume expansion could result in the defect creation identified with the SWE.

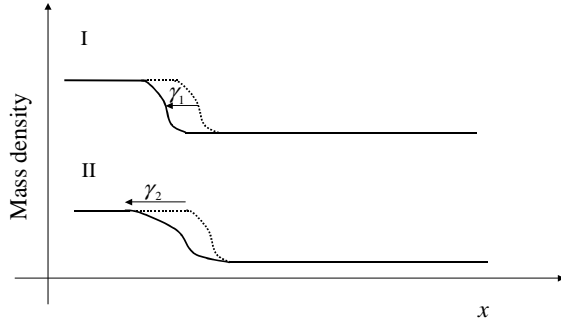


Fig. 2. Two types of boundary motion that increase disorder.

The time evolution of the observed volume expansion is roughly exponential, or stretched exponential [6], as is typically the case for metastable phenomena in amorphous materials. In the context of this model, a single exponential saturation of the volume expansion means that the rate of domain boundary motion is equal to $\frac{\gamma_s - \gamma(t)}{\tau}$, where $\gamma(t)$ is a generalized distance over which a boundary has moved at time t , γ_s is its saturated value, and τ is the time constant. If

we identify γ as proportional to the density of microscopic sites N in or at the edge of the boundaries that have undergone configurational change, then $\frac{dN}{dt} = \frac{N_s - N}{\tau}$. In general, the saturated density N_s will be a function of illumination intensity and temperature.

DISCUSSION

The general concepts of the weak-bond (WB) breaking model [7] are entirely consistent with this model, wherein, the light-induced metastable DB's are stabilized by local H reconfiguration. In the context of this model, shifts of the domain boundaries lead to redistribution of strain which could be responsible for creating the small fraction of DB's (spatially uncorrelated with H) relative to the much larger number of non-defect metastable sites. This model may also explain the observed defect saturation behavior that is not directly predicted by the WB kinetics that follow from populations of defect states [7], since steric constraints on boundary motion could play a limiting role. Other features of the SWE that are consistent with this model include: 1) the volume expansion and defect creation follow the same time evolution [6]; 2) the SWE is not very efficient, i.e. 10^{24} cm⁻³ recombination events are required to produce 10^{17} cm⁻³ new defects [8]: this may be understood by our model since the vast majority of recombination-driven structural changes do not produce defects, and defect creation is limited to the domain boundary regions. Various photostructural changes have also been observed [9] which lend support to a picture of gross structural changes that "precede" defect creation.

ACKNOWLEDGMENTS

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